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Mass Balance for Mercury in the San Francisco Bay Area

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We have developed and illustrated a general regional multi-species model that describes the fate and transport of mercury in three forms, elemental, divalent, and methylated, in a generic regional environment including air, soil, vegetation, water, and sediment. The objectives of the model are to describe the fate of the three forms of mercury in the environment and to determine the dominant physical sinks that remove mercury from the system. Chemical transformations between the three groups of mercury species are modeled by assuming constant ratios of species concentrations in individual environmental media. We illustrate and evaluate the model with an application to describe the fate and transport of mercury in the San Francisco Bay Area of California. The model successfully rationalizes the identified sources with observed concentrations of total mercury and methyl mercury in the San Francisco Bay Estuary. The mass balance provided by the model indicates that continental and global background sources control mercury concentrations in the atmosphere but that loadings to water in the San Francisco Bay Estuary are dominated by runoff from the Central Valley catchment and remobilization of contaminated sediments deposited during past mining activities. The model suggests that the response time of mercury concentrations in the San Francisco Bay Estuary to changes in loadings is long, on the order of 50 years.

Introduction

Multimedia mass balance models are increasingly recognized as indispensable tools for developing a quantitative understanding of emissions, fate, transport, and the ultimate sinks of environmental contaminants. When applied at the regional, national, continental, or global scale, these models provide a framework for quantitatively accounting for sources, observed concentrations, and the ultimate fate of environmental contaminants. This class of models provides academic researchers, industry, policy makers, and regulators with quantitative tools for assessing the impacts of possible alternative chemical emission scenarios on environmental quality (*1*, *2*).

Currently available regional mass balance models (i.e., refs *3*−*5*) are most appropriate for nonionizing organic chemicals and nonspeciating metals. These models explicitly account for the fate and transport of a single chemical. When the contaminant of interest undergoes a chemical transformation that alters its environmental partitioning behavior, it is no longer tracked by the model and is considered to have been irreversibly removed from the modeled environment. This characteristic makes these models inappropriate for describing the fate and transport of environmental contaminants that may exist as several interconverting chemical species. Mercury is a prominent example of an environmental contaminant that converts between chemical forms with very different environmental fate properties.

Diamond and co-workers (*6*, *7*) have modeled the fate of mercury in aquatic systems using a mass balance model framework that accounts for three interconverting species groups. More recently, Cahill et al. (*8*) have proposed a comprehensive regional mass balance framework that simultaneously accounts for partitioning and kinetics of interconversion of multiple chemical species in the whole environment, and Mackay and Toose (*9*) have proposed a general framework that allows mass balance calculations for multi-species chemicals to be derived from single-species model calculations.

In this paper, we follow the approach of Mackay and Toose (*9*) for solving multi-species mass-balance equations to develop a regional multi-species model designed specifically for mercury. The model simultaneously describes the fate and transport of elemental mercury (Hg^0), a divalent mercury species group (Hg^{2+}), and a methylated mercury species group (MeHg) in a generic regional environment including air, soil, vegetation, water, and sediment. The current model is therefore distinct from regional mercury models that address atmospheric dispersion and deposition of mercury (*10*−*12*). The model is structured to describe the fate of the three different forms of mercury in a regional environment and to determine the dominant physical sinks that remove mercury from this system. Chemical transformation rates between elemental mercury and divalent and methyl mercury species groups are determined by difference from the mass balance equations, assuming constant concentration ratios for each environmental media. The goals of this paper are to both develop and evaluate the model by compiling a mass balance for mercury in the San Francisco Bay Area, CA, a region with a well-characterized mercury contamination problem.

The San Francisco Bay Estuary is contaminated with an array of industrial and agricultural chemicals, including mercury (*13*). Mercury concentrations in fish from the Estuary are high enough to trigger fish consumption advisories from the California Office of Environmental Health Hazard Assessment (*14*). Elevated mercury concentrations in bird eggs may be contributing to abnormally high rates of reproductive failure (*15*). In contrast to many aquatic systems in North America that are threatened by mercury contamination primarily as a result of atmospheric deposition, the major sources of mercury to the Estuary are surface water transport from upstream watersheds and erosion of contaminated sediments. Mining practices during the Gold Rush era (∼1850−1900) introduced large amounts of mercury to California watersheds, and as a result of their biogeochemical behavior, these watersheds are a continuing source of mercury to the of the tributaries of the San Francisco Bay Estuary.

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Theory

The regional fate and transport model developed here follows the multi-species "multiplier-method" fugacity calculations outlined by Mackay and Toose (*9*) and is closely related to the aquivalence-based model of Diamond (*6*). The text by Mackay (*2*) describes the fundamentals of mass balance models using the fugacity concept. Mercury transport rates by diffusion and advection are described using *D* values (mol Pa^{-1} h^{-1}) such that the product *Df* is the transport rate (mol h^{-1}), where *f* (Pa) is the chemical's fugacity. The key assumption in assembling the model is that the temporally and spatially averaged ratios of concentrations (and fugacities) of the individual mercury species are constant in each bulk model compartment. This assumption will be valid when chemical reactions for interconversion of the various mercury species are fast relative to the rates of transport in and out of the environmental compartment under consideration and across the boundaries between environmental compartments. However, it is not a requirement that the interconversion reactions are fast. In systems that are near steady-state, the concentration ratios will be constant and can be estimated from environmental monitoring data.

Mass balance equations for total mercury (ΣHg) are formulated using elemental mercury (Hg^0) as the key species (*9*), recognizing that it is a multi-media contaminant that partitions to all accessible environmental compartments. Transport rates (*N*, mol h^{-1}) of total mercury can then be expressed as

$$N = f_E D_E + f_D D_D + f_M D_M \quad (1)$$

$$N = f_E D_E\,(1 + (f_D/f_E)(D_D/D_E) + (f_M/f_E)(D_M/D_E)) \quad (2)$$

where the subscripts E, D, and M refer to elemental mercury, divalent mercury, and methyl mercury species groups, respectively. The assumption of constant ratios of species concentrations implies that the ratios of fugacities and *D* values for the species are also constant. Therefore, the transport rates for total mercury can be expressed as the product of a transport rate calculated for the key species, elemental mercury, and a constant (*C*) specific to each compartment that accounts for transport of the other two species

$$N = f_E D_E C \quad (3)$$

where

$$C = (1 + (f_D/f_E)(D_D/D_E) + (f_M/f_E)(D_M/D_E)) \quad (4)$$

The mass balance equations for the three species of mercury can be solved simultaneously by first assembling a conventional single-species model for Hg^0, then deducing the *D* values and process rates for the other two species and total mercury.

A complication arises for the divalent mercury species group (Hg^{2+}) in that it does not have a measurable vapor pressure; therefore, the fugacity capacity (*Z*, mol m^{-3} Pa^{-1}) of pure air for this species cannot be defined (*2*). We overcome the problem by setting the *Z* value of pure air for Hg^{2+} to zero and that in water arbitrarily to 1 mol m^{-3} Pa^{-1}. This has the effect of normalizing the environmental partitioning of this species group to water rather than air, as is done in the standard fugacity approach. Thus, the equations describing Hg^{2+} effectively use aquivalence (*6*) as the criterion of equilibrium; however, we retain the units of Pa to ensure that the equations describing the fate of different species have the same units. *Z* values for Hg^{2+} for all other environmental media (except atmospheric aerosols) are deduced from estimated environmental partition coefficients and the arbitrarily defined *Z* for water. The total capacity of air in the regional environment for Hg^{2+} (the product of the volume of air and its *Z* value) is defined to be zero, and diffusion of this species into air does not occur.

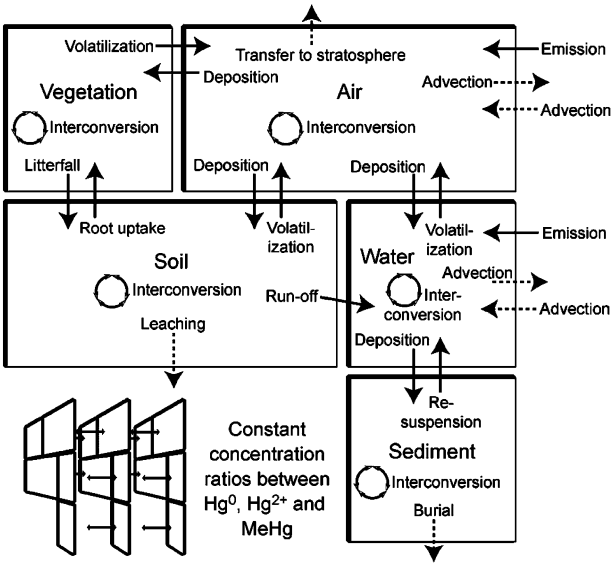

FIGURE 1. Generic multimedia model environment, including a representation of the relationship between the different mercury species groups. Arrows represent transfer and transformation processes described in the model.

We account for the divalent mercury species group in the atmosphere only as a nonvolatile pollutant associated with aerosols. A set of rate constant equations that is independent of the rest of the model is used to describe atmospheric transport and deposition of this particle-associated Hg^{2+}. Direct atmospheric emissions and background inflow of particulate Hg^{2+} are balanced by rates of advective outflow and wet- and dry-particle deposition. We account for divalent mercury that is deposited to surface media as a source term in the fugacity equations. Therefore, when divalent mercury is deposited from the atmosphere, we assume that it takes on the species concentration ratios defined for the receiving compartment.

The current model seeks to describe long-term average mercury dynamics in a generic regional environment. It is not appropriate for describing episodic mercury depletion events in the atmosphere characterized by rapid conversion of Hg^0 to Hg^{2+}. However, the long-term impact of such events on atmospheric deposition rates of mercury on the regional scale can be modeled if appropriate average species concentration ratios are specified in the atmosphere.

Figure 1 shows the generic regional environment as conceived in the model. Arrows in the diagram represent transfer processes and pathways available to the three species groups of mercury. Mass balance equations determine the inventory and concentrations of each species group in each compartment. The model software is coded as a Visual Basic add-on to Microsoft Excel, and both steady-state and dynamic (time varying) solutions have been implemented. We focus our attention here on steady-state solutions describing current mercury loadings to the San Francisco Bay Area.

To represent mercury partitioning and dynamics in plants and forest foliage, we include a generic vegetation compartment in the regional mass balance. The role of vegetation in the fate of mercury in the environment is an area of active research, and the current model includes a provisional attempt to quantify the processes involved. Experimental and modeling studies indicate that plants can mobilize mercury from contaminated soils into the atmosphere (*16*) and that forest foliage can scavenge mercury from the

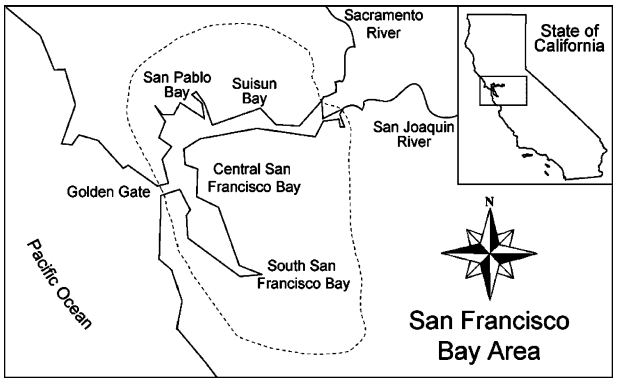

FIGURE 2. Map of the San Francisco Bay Area. The dashed line represents the approximate boundaries of the model domain.

atmosphere (*17*). Our model describes diffusive exchange between vegetation and atmosphere using a two-resistance model (*18*). Resistance on the plant side controls the overall mass transfer coefficient for diffusive exchange of Hg^0, and transfer through the stomata plays an important role (*16*). Particulate mercury can be deposited to the vegetation surface from the atmosphere, and mercury dissolved in interstitial water in soils is taken up through roots assuming negligible resistance at the root−water interface. Mercury uptake by vegetation is balanced by diffusion to the atmosphere and transport to soils by litterfall.

Site Description

The San Francisco Bay Area, CA is a nine-county metropolitan area that surrounds the San Francisco Bay Estuary. The Bay Area has a population of over 7 million including the cities of San Francisco, San Jose, and Oakland and is the fifth largest metropolitan area in the U.S. Figure 2 is a map of the Bay Area including sub-basins within the Bay. The Estuary is the outlet of the Sacramento and San Joaquin Rivers, which drain California's Central Valley representing 40% of the entire area of the state.

Regional environmental properties and associated uncertainties, expressed as confidence factors, used as inputs to the mercury fate and transport model are shown in Table 1. The confidence factor (Cf) defines the 95% confidence limits around a median value for each input parameter due to uncertainty and variability. We estimate this factor assuming that the parameter variance due to variability and uncertainty can be represented by a log-normal distribution (*19*). Thus, 95% of the possible values for a given parameter (P) falls between P/Cf and $P \times$ Cf.

The modeled regional environment is defined by the watershed boundaries for the San Francisco Bay Estuary except for the Sacramento and San Joaquin Rivers, which enter the model domain at the eastern end of Suisun Bay (Figure 2). Because of the importance of the Estuary as a defining feature of the Bay Area regional environment, the availability of extensive monitoring data (*25*), and the use impairments caused by the fish consumption advisories, significant effort was devoted to selecting optimal parameters and confidence factors to describe the hydrodynamics and sediment budget of the Bay.

When parametrizing the model with region-specific data, we faced a tradeoff between complexity and reliability. The available information on mercury loadings and the current understanding of mercury kinetics in the Estuary favored a single-region model as optimum for transparently assessing the overall mass balance in the system. But, the use of a single-region model for an estuary with a high degree of variability in environmental conditions complicates the specification of some of the landscape and hydrologic parameters that characterize this system. The key advantage of a single-region model is transparent compilation of the mass balance and the ability to perform an uncertainty analysis to characterize the influence of highly variable and/or uncertain input parameters. The model therefore provides an initial mass balance that can be refined as necessary.

Of particular note is the value of the single-region model for assessing the descriptive power of the model framework and for evaluating the impact of future refinements to the model and/or to the quantity and quality of available data.

TABLE 1. Regional Environmental Properties and 95% Confidence Factors (Cf) for the San Francisco Bay Area Region

parameter name	median value	Cf	ref
Dimensions			
region area (km^2)	10215	1	*20*
% surface covered by water	12.1	1.05	*20*
% soil covered by vegetation	80	1.1	*a*
leaf area index (m^2/m^2)	3	2	*18*
vegetation mass per square meter (kg/m^2)	1	2	*18*
air compartment height (km)	1	1.5	*2*
water depth (m)	6.9	1.15	*21*
soil depth (cm)	10	2	*2*
active sediment layer depth (cm)	15	3	*22*
Volume Fractions for Subcompartments			
suspended particles in water	0.00001	16	*b*
air in soil	0.2	1.5	*2*
water in soil	0.3	1.5	*2*
sediment pore water	0.53	1.6	*b*
water in vegetation	0.75	1.1	*18*
Temperature Conditions			
average environmental temperature (°C)	15	1.1	*23*
Residence Times (days)			
Air	0.39	3	*c*
Water	34	3	*d*
average vegetation cycle	365	1	*18*
Transport Velocity Parameters (m/h)			
air side air−water MTC[e]	5	3	*2*
water side air−water MTC	0.05	3	*2*
rain rate	0.0000605	2	*20*
aerosol deposition	10.8	3	*2*
soil air phase diffusion MTC	0.02	3	*2*
soil water phase diffusion MTC	0.00001	3	*2*
soil solids convection	0.000000454	3	*24*
soil air boundary layer MTC	5	3	*2*
sediment−water diffusion MTC	0.0001	3	*2*
suspended particle deposition	0.00000262	3	*f*
sediment resuspension	2.47×10^{-6}	3	*f*
soil water runoff	0.00005	3	*2*
soil solids runoff	0.00000001	3	*2*
diffusion to stratosphere	0.01	3	*4*
leaching from soil	0.00001	3	*2*
air side air−vegetation MTC	10	3	*18*
vegetation side air−vegetation MTC	0.000005	3	*g*
vegetation water uptake velocity	0.0008	3	*18*
Rain Scavenging Parameters			
rain scavenging ratio	110000	3	*2*
fraction of rain intercepted by foliage	0.1	2	*18*

[a] Estimated from satellite image at http://asterweb.jpl.nasa.gov/gallery/gallery.htm?name=SF. [b] Geometric mean and confidence factor from RMP data (*25*). [c] Estimated based on an assumed 3 m/s long-term average windspeed. [d] Estimated based on a range of 1−90 days reported in Abu-Saba and Tang (*20*) and the sediment budget reported by Krone (*26, 27*). [e] MTC: mass transfer coefficient. [f] Estimated based on sediment budget by Krone (*26, 27*). The sediment resuspension MTC was limited in the Monte Carlo analysis such that sediment resuspension could not exceed suspended particle deposition. The sediment burial MTC is calculated as the difference between suspended particle deposition and sediment resuspension MTCs. Net sediment burial was calculated to be zero in 48% of Monte Carlo iterations. [g] Estimated based on the relative rates of evasion and litterfall reported by Hintelmann et al. (*28*)

TABLE 2. Mercury Emission Parameters for the San Francisco Bay Area (*15*, *20*, *30*, *31*)

background inflow concentrations	median	Cf[a]
Hg^0 + MeHg in background air (ng/m^3)	2.1	1.5
particulate Hg^{2+} in background air (ng/m^3)	0.1	3

mercury sources (kg/year)	Hg^0	Hg^{2+} species group	MeHg species group	Cf
Air	370	0	0	3
Water	0	736[b]	1.3	3
erosion of contaminated sediments	0	460	0	3

[a] Cf: 95% confidence factor. [b] Composed of 19 kg/year from wastewater discharges, 277 kg/year from within-basin watershed runoff, and 440 kg/year from Central Valley watershed sources (*15*).

This approach allows us to prioritize new data to produce the most efficient reduction in uncertainty of the model outputs. A disadvantage of the single-region model is that it requires selection of a single best estimate value to describe an estuary with characteristics that are highly variable in space and time in the real system. For example, some areas of the Estuary are experiencing net deposition of sediments from the water column, while others are undergoing net erosion (*27*). Similarly, the concentration of suspended sediments in the water column varies over more than 2 orders of magnitude between areas near the outlet of major rivers and the mouth of the Golden Gate (*25*). As a result, the confidence factors for input parameters must be selected to describe characteristics of the Estuary that are highly spatially variable. We based the average sediment budget used in the model on the work of Krone (*26*, *27*). The water and sediment budgets have been harmonized so that the hydrodynamics of the system are at steady-state (i.e., the net flows of water and sediment into the system are balanced by flows out of the system and burial in the case of sediment solids).

Regional Mercury Emissions. Mercury enters active circulation in the San Francisco Bay Area by (a) direct local emissions, (b) advective inflow in the atmosphere and from the Central Valley rivers, (c) remobilization of contaminated sediments, and (d) erosion of mercury-containing soils. Suisun Bay and San Pablo Bay are repositories for contaminated sediments that were deposited in the 1850s through the 1880s from hydraulic mining operations in the Sierra Nevada Mountains. Hydraulic mining techniques used at this time required large volumes of water to strip hillsides of soil. Gold was extracted from the resulting slurry by settling in sluices lined with elemental mercury that captured fine gold particles (*29*). The legacy of these operations is mercury contamination in the sediments of the San Francisco Estuary as well as the sediments upstream in the San Joaquin and Sacramento watersheds. Therefore, major sources of mercury for the San Francisco Region include releases from sediments in the Estuary and from sediments upstream that enter the Estuary through the Sacramento and San Joaquin Rivers. In addition to historically elevated levels of mercury in the Estuary and river sediments, the hills immediately surrounding the Estuary have naturally high concentrations of mercury, and the area was home to mercury mining operations up to the 1970s (*15*).

As part of its development of an estimated total maximum daily load (TMDL) for mercury to the San Francisco Bay Estuary, the California Regional Water Control Board has estimated current mercury sources to the Bay Area. Direct loading estimates for the San Francisco Bay Estuary and their associated uncertainty ranges were first reported to the U.S. EPA on June 30, 2000 (*20*). Estimates of loading to the San Francisco Bay Estuary were revised to be slightly lower in a more recent TMDL report (*15*). For the purposes of this modeling exercise, the most recent loading estimates have been used with uncertainty ranges estimated from data presented in both reports. The flux of MeHg entering the Bay from the Sacramento and San Joaquin Rivers is taken from the study by Choe and Gill (*30*). Emission estimates are summarized in Table 2.

TABLE 3. Reported Mercury Concentrations and Fluxes in the Bay Area Region and Associated 95% Confidence Factors (Cf)

	total mercury		methyl mercury	
environmental medium	median	Cf	median	Cf
dissolved in water (ng/L)[a]	1.25	4.65	0.033	11.2
bulk water (ng/L)[a]	9	11.1	0.0435	6
sediment (ng/g of dry weight)[a]	250	4.42	0.426	10.8
bivalve (ng/g of dry weight)[a]	251	2.09		
air (ng/m^3)[b]	2.1	1.5		
rain (ng/L)[b]	8	1.22		
depositional flux to water (μg/m^2/year)[b]	19	2		

[a] SFEI (*25*). [b] Tsai and Hoenicke (*31*).

Direct mercury inputs to the atmosphere in the San Francisco Bay Area have been estimated to be 370 kg of total mercury per year from a combination of stationary and mobile combustion sources, breakage of consumer products such as fluorescent lamps, and emissions from abandoned mine sites (*20*). The speciation of mercury released to the atmosphere is not specified in the TMDL reports (*15*, *20*); therefore, we assume that 100% of local mercury sources to the atmosphere is in the form of elemental mercury. In addition, air entering the Bay Area air basin is assumed to be contaminated with total mercury at a concentration of 2.1 $\pm$ 0.8 ng/m^3, reflecting the background contaminant burden due to large-scale cycling of natural and anthropogenic mercury (*31*).

Regional Mercury Concentrations in the Environment and Biota. Total mercury concentrations in water, sediment, and bivalves in the San Francisco Bay Estuary have been monitored since 1993 by the Regional Monitoring Program (RMP) under the direction of the San Francisco Estuary Institute (*25*). Total mercury concentrations in the San Francisco Bay ecosystem have not shown any discernible temporal trend during this 10 year monitoring program, indicating that the system is currently near steady-state. In 2000, the RMP began monitoring methyl mercury as well as total mercury in the Estuary. Median total mercury and methyl mercury concentrations from the RMP data set averaged over the whole bay are shown in Table 3, along with 95% confidence factors of observed concentrations from different sites and different sampling years.

Tsai and Hoenicke (*31*) reported mercury concentrations in ambient air from three sites in the San Francisco Bay Area during the year 2000 and estimated the depositional flux of mercury to the Estuary. Median concentrations observed in this study and confidence factors are also shown in Table 3, along with their estimate of the depositional flux from the atmosphere.

TABLE 4. Partition Coefficients (*K*) and Species Concentration Ratios for Mercury in the San Francisco Bay Area and Associated 95% Confidence Factors (Cf)

	Hg^0		Hg^{2+} Species Group		MeHg species group	
property	median	Cf	median	Cf	median	Cf
molecular weight (g/mol)	200.6	1	200.6	1	200.6	1
K air/water	0.32[a]	3	0	1	1.5×10^{-5}[b]	3
K vegetation flesh/water	1[c]	3	100[c]	3	500000[c]	3
K soil solids/water	20000[d]	3	100000[d]	3	5000[d]	3
K sediment solids/water	20000[a]	3	100000[a]	3	5000[a]	3
K suspended solids/water	30000[a]	3	1000000[e]	3	50000[e]	3
K bivalve/water	1[a]	3	1000[a]	3	1000000[e]	
pure phase concentration ratios						
air (vapor phase)	1	N/A	0	1	1×10^{-6}[c]	3
water (dissolved phase)	1	N/A	96[e]	3	3[e]	3
soil (solid phase)	1	N/A	998[f]	3	1[f]	3
sediment (solid phase)	1	N/A	588[e]	3	1[e]	3
vegetation flesh (solid phase)	1	N/A	989[c]	3	10[c]	3

[a] Mackay et al. (*32*). [b] Diamond (*6*). [c] Estimated. [d] Assumed equal to *K* sediment solids/water. [e] Calculated from RMP data from San Francisco Bay (*25*). [f] Estimated based on sediment solids concentration ratios.

Partition Coefficients and Concentration Ratios for Mercury Species. In Table 4, we provide values of dimensionless partition coefficients and concentration ratios, and their associated confidence factors, for the three mercury species groups. When possible, we have estimated partition coefficients and concentration ratios from monitoring data gathered in the San Francisco Bay Area region. In this regard, the model has been tuned to provide the most accurate possible description of partitioning and speciation of mercury in the system.

Model Uncertainty Analysis and Model Evaluation. Because models are developed for specific purposes, they are not true or valid in a general sense but can become useful by accumulating confidence through calibration, verification, and evaluation exercises. In this section, we explain the process we used to characterize the uncertainty in the model results and to evaluate its performance relative to available benchmark measurements. We carried out an uncertainty analysis using standard error propagation methods and evaluated model performance against observed mercury concentrations in the San Francisco Bay region.

Uncertainty analysis of the model's description of mercury fate in the Bay Area was carried out by Monte Carlo analysis using the confidence factors shown in Tables 1, 2, and 4 to represent uncertainty and variability in input parameters. We used the Crystal Ball Software package with 5000 trials and standard Monte Carlo sampling to propagate input variance to outcome variance. We used the results of this process to construct the range and likelihood of media-specific mercury species concentration values. In Figures 3 and 4, we compare modeled and measured 95% confidence intervals for ΣHg and MeHg concentrations in the Bay Area. In Figure 3, we compare our model estimate of the depositional flux of ΣHg to the Estuary with the previous estimate made by Tsai and Hoenicke (*31*). The diagonal line in Figures 3 and 4 is provided for reference indicating a 1:1 relationship between modeled and observed concentrations and fluxes of Hg in the system.

Figures 3 and 4 indicate that the model is providing a satisfactory overall description of mercury loadings, fate, and transport in the Bay Area region that is consistent with observations. In all cases, the 95% confidence interval in the model results overlaps the 95% confidence interval in the observed concentrations or the previous estimate of depositional flux of total mercury.

It is noteworthy that the confidence intervals in both the model results and the measurement data are wide, spanning over 2 orders of magnitude in some cases for ΣHg and in all cases for the MeHg species group. These large confidence intervals are a result of the spatial and temporal heterogeneity of the Estuary system and uncertainty and variability associated with the Bay-wide suspended particle and sediment balance. The single water compartment in the model averages depositional zones near the major river inputs and oceanic conditions at the mouth of the Golden Gate. Because of this variability in conditions, the variance in suspended particulate concentration (an input to the model) is estimated at a factor of 16. The active depth of sediments in the Bay is another highly uncertain and variable input parameter that drives the wide confidence intervals in the model outputs. The central estimate of active sediment mixing depth (15 cm) is based on a value selected for a similar model applied to PCBs (*22*) and a single study at one location in the San Francisco Bay (*33*). It is assigned a confidence factor of 3 to represent uncertainty associated with estimating a value from only one measurement and variability in sediment bed shear throughout the system.

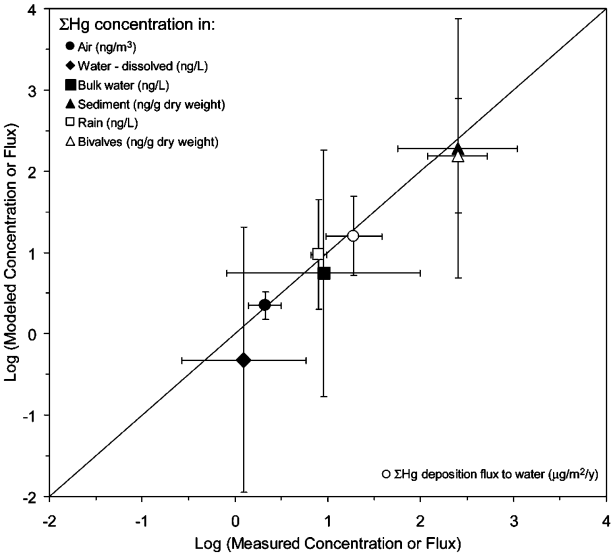

FIGURE 3. Comparison of modeled and observed concentrations and fluxes of total mercury in the Bay Area.

Species-Specific Mass Balances for Mercury. Figure 5 shows steady-state mass balance diagrams for Hg^0, the Hg^{2+} species group, the MeHg species group, and ΣHg, using the median values of all input parameters. Fluxes are shown in kg/year and summed for each process to calculate fluxes of ΣHg. Inspection of Figure 5 shows that the dominant fate

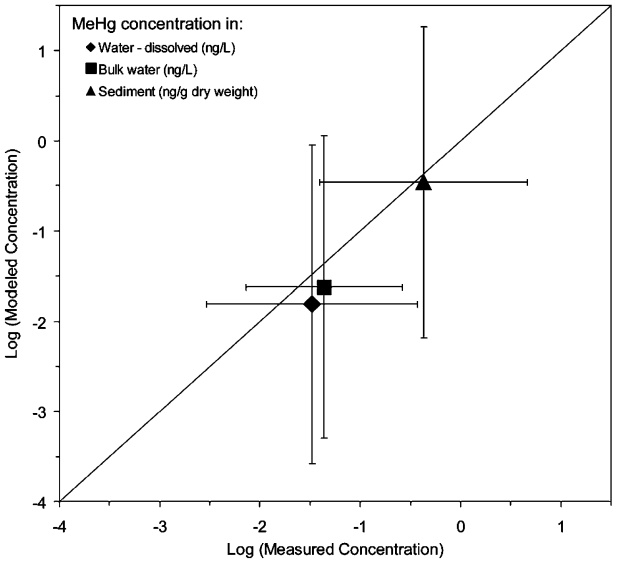

FIGURE 4. Comparison of modeled and observed concentrations of methyl mercury in the Bay Area.

and transport processes differ considerably for the three species groups of mercury.

The model mass balance indicates that elemental mercury loading to the San Francisco Bay region is dominated by inflow of background air, which contributes over 50 times more mercury loading than local emissions to the atmosphere. However, background inflow is balanced by advection out of the region, which slightly exceeds inflow, indicating that the Bay Area region provides a net input of atmospheric Hg^0 to the global environment. After direct emission, the most important regional contribution of Hg^0 to the atmosphere is volatilization from vegetation. The modeled mass balance indicates that divalent mercury (Hg^{2+}) species are taken up by vegetation from soils and as a result of particulate deposition from the atmosphere. The Hg^{2+} is then converted to Hg^0 in the vegetation compartment and subsequently volatilized to the atmosphere. Leonard et al. (*16*) have examined the possible role of vegetation as a pathway for mercury evasion from contaminated soils to the atmosphere. Our proposed model also indicates that vegetation may act as a medium for the conversion of Hg^{2+} species into Hg^0, which is then subject to global-scale transport in the atmosphere.

Despite the large fluxes through the atmosphere, the largest single reservoir of Hg^0 in the San Francisco Bay regional environment is in the sediment compartment. The model suggests that elemental mercury is produced in sediments by conversion from Hg^{2+} species that were deposited on particles from the water column. Net production in sediments drives a flux of Hg^0 from sediment to water, where it is converted back to Hg^{2+} species. Volatilization of Hg^0 from the Bay to the atmosphere is approximately balanced by atmospheric deposition. Although the model indicates that a high percentage of the Hg^0 burden in the region resides in soil and sediment, the concentration of Hg^0 in these compartments is very low relative to Hg^{2+}, as indicated by the concentration ratios shown in Table 4.

Similarly to Hg^0, there is a significant flux of Hg^{2+} species through the Bay Area region in the atmosphere. The dominant deposition process from the atmosphere for the entirely particle-associated Hg^{2+} species is scavenging by vegetation. However, atmospheric deposition of the Hg^{2+} species is a very minor component of total loadings to the Estuary, which are dominated by the sources identified in the TMDL reports (*15*, *20*). Soil and the sediments of the Estuary house the bulk of the regional inventory. In the aquatic system, the most prominent feature of the Hg^{2+} fate is cycling between water column and sediments. An average Hg^{2+} atom undergoes 10 cycles of deposition and resuspension during its residence time in the Bay. As a result of the close coupling between the water and the sediment system, resuspension is the dominant source to the water compartment, indicating that contamination in the sediments is controlling Hg^{2+} concentrations in estuary water.

Methylated mercury species are of particular concern in aquatic ecosystems because of their tendency to bioaccumulate to unacceptably high levels in food webs. The Bay Area regional mass balance indicates that a small net production of MeHg species occurs in sediments (Figure 5). Methyl mercury production in sediments is consistent with bacterial methylation of Hg^{2+} species. The net methylation rate calculated by the model in sediment is small, less than 2 kg/year. If substantial methylation is occurring in wetlands within the Bay, the model indicates that it is approximately balanced by demethylation reactions in other parts of the system. This interpretation is consistent with Choe and Gill (*30*), who estimated 0.6 kg/year net destruction of monomethyl mercury in the northern reach of the San Francisco Bay based on analysis of water samples at different locations.

The mass balance of ΣHg in the Bay Area is determined almost entirely by the dynamics of the Hg^{2+} species group, the most prevalent species group in all compartments of the system except the atmosphere. There is net atmospheric deposition of ΣHg to soils, water, and vegetation in the region. Because of the large flux of Hg^0 through the atmosphere, the overall regional residence time of ΣHg is only 6.3 years; however, residence time in the Estuary is much longer (~50 years) and is determined by the residence time of Hg^{2+} associated with sediments in the system.

The results of the uncertainty analysis (Table 5) illustrate the controlling influence of sediment dynamics on the fate and transport of mercury in the Estuary. Aside from the rate of direct emission of Hg^{2+} species to water, the model parameters that control variance in calculated mercury concentrations in water and sediment in the Estuary are all parameters associated with the description of the sediment budget of the system. In particular, the response time of the water−sediment system to changes in mercury loading is controlled to a large extent by the active sediment layer mixing depth and the relative rates of sediment burial versus removal to the ocean by resuspension and advection in bulk water. To a large extent, the uncertainties associated with the current model are determined by uncertainty and variability associated with attempting to assign single, Bay-wide estimates to these parameters.

Discussion

The current model is relatively simple in form and is designed to provide an overall accounting of sources and sinks in the San Francisco Bay region. The lack of spatial resolution introduces a high degree of variance in calculated mercury concentrations because of the spatial heterogeneity of the real system. The model has, however, demonstrated reliability in making large-scale mass balance estimates for mercury in a way that allows policy makers to understand the relative importance of various emissions sources and loss mechanisms. In many modeling studies of this type, data available for model evaluation are the limiting factor determining the spatial resolution of the assessment. In this case, the quality and quantity of monitoring data becoming available from the San Francisco Estuary Institute RMP program provide future opportunities to refine the current model by introducing more spatial resolution within the Estuary. With sufficient calibration data, a spatially resolved model could

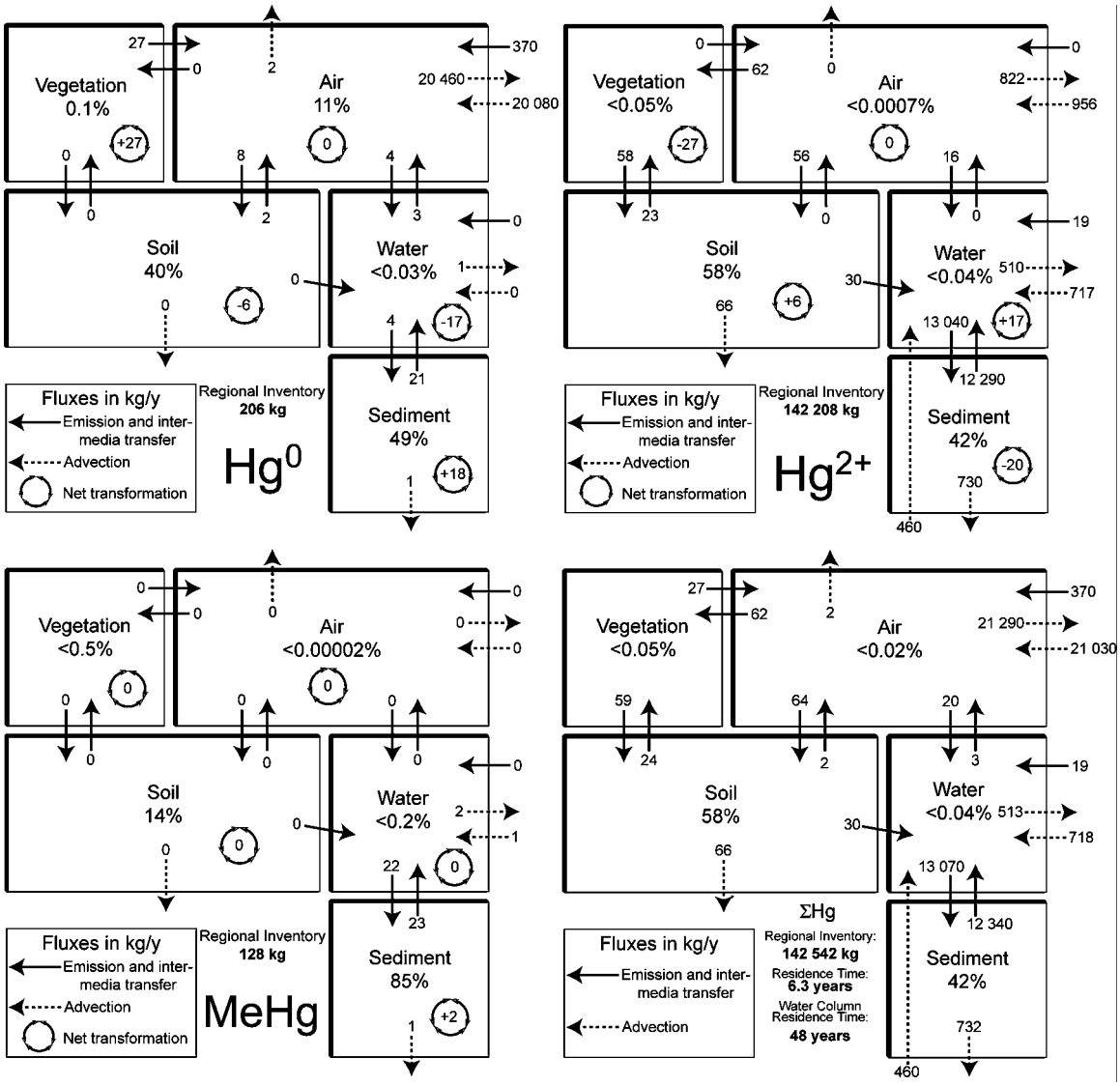

FIGURE 5. Steady-state mass balance of elemental mercury (Hg^0), divalent mercury species (Hg^{2+}), methyl mercury species (MeHg) and total mercury (ΣHg) in the San Francisco Bay Area. Fluxes are rounded to the nearest 1 kg/y or 4 significant digits. Percentages are of the total quantity of each mercury species.

TABLE 5. Percent Contribution to Variance in Modeled Total Mercury Concentrations and Persistence in the San Francisco Bay Estuary

	percent contribution to variance in output		
input parameter	ΣHg concentration in water (%)	ΣHg concentration in sediment (%)	ΣHg persistence in water − sediment system (%)
suspended particle deposition velocity	44	44	46
sediment resuspension velocity	30	26	26
volume fraction suspended particles	6	13	14
water residence time	6	2	2
Hg^{2+} emission rate to water	13	10	<0.1
active sediment layer depth	<0.1	<0.1	9
total	99	95	97

reduce uncertainties in model results and provide mercury concentrations and response times to changes in loadings for sub-basins within the Bay. Moreover, because the imports from the Central Valley are attributable to historical loads in the sediments of the Sacramento and San Joaquin catchments, there is a need to incorporate the long-term behavior of these river systems in future modeling efforts.

The development of a reliable spatially resolved mercury mass balance model for the San Francisco Estuary system will require site-specific studies of sediment dynamics in the system. Without this information, spatial resolution cannot reduce total variance in model results. Sediment dynamics studies that provide a more refined understanding of active sediment layer depth and sediment deposition and resuspension rates will also contribute to improved understanding of the dynamics of other particle associated contaminants in the system, such as highly chlorinated polychlorinated biphenyls (*22*).

We suggest that the first priority for refining the current model is increasing the spatial resolution in the estuary system. Future models might also include a kinetic description of species interconversion reactions; however, the option to retain the assumption of constant species concentration ratios in model compartments should be retained. This assumption makes the modeling process much easier to manage and avoids the need for rate constants that describe media specific transformations among the species groups. Since these rate constants are not currently available, a model that requires these parameters will have large inherent uncertainties. Therefore, a refined model that adds both more spatial resolution and a kinetic description of species interconversion could actually increase rather than decrease uncertainties.

In summary, the regional fate and transport model presented here successfully reconciles identified sources with observed concentrations of total mercury and methyl mercury in the San Francisco Bay area. The mass balance provided by the model indicates that continental and global background mercury concentrations control levels in the atmosphere of the Bay Area but have little impact on surface water concentrations of total mercury in the Estuary. Loadings to the San Francisco Estuary are dominated by runoff from the Central Valley and remobilization of contaminated sediments deposited during past mining activities. Moreover, the imports from the Central Valley are attributable to historical loads in the sediments of the Sacramento and San Joaquin watersheds. The model framework developed here is general and can be applied to other systems to test its robustness, including systems where mercury inputs are dominated by atmospheric deposition.

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